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20 (71) Applicant: 301021533
 National Institute of Advanced Industrial Production and Technology

25 (71) Applicant: 000000033
 Asahi Kasei K.K.
 2-6 Doshimahama-1-chome, Kita-ku, Osaka-shi, Osaka-fu, Japan, Japan

30 (71) Applicant: 000000044
 Asahi Glass K.K.
 12-1 Yurakucho-1-chome, Chiyoda-ku, Tokyo-to, Japan

(71) Applicant: 000157119

Kanto Denka Kogyo K.K.

2-1 Marunouchi-1-chome, Chiyoda-ku, Tokyo-to, Japan

(71) Applicant: 000002004

Showa Denko K.K.

5 13-9 Shibadaimon-1-chome, Minato-ku, Tokyo-to, Japan

(71) Applicant: 000002200

Central Glass K.K.

5253 Oazaokiube, Ube-shi, Yamaguchi-ken, Japan

(71) Applicant: 000002853

10 Daikin Kogyo K.K.

Umeda Central Building, 4-12 Nakazakimishi-2-chome,
Kita-ku, Osaka-shi, Osaka-fu, Japan

(71) Applicant: 000003034

Toa Gosei K.K.

15 14-1 Nishishinbashi-1-chome, Minato-ku, Tokyo-to, Japan

(71) Applicant: 000174851

Mitsui DuPont Fluorochemical K.K.

5-18 Sarugakucho-1-chome, Chiyoda-ku, Tokyo-to,
Japan

20 (72) Inventor: Junji MURATA

c/o New Standard Cold Catalyst Etc. Project Laboratory,
National Institute of Advanced Industrial Production and
Technology, Hongo Wakai Building 6F, 2-40-17 Hongo,
Bunkyo-ku, Tokyo-to, Japan

25 (72) Inventor: Toshihiko NICHIAKI

6-17 Okubo -4-chome, Narashino-shi, Chiba-ken, Japan

(72) Inventor: Akira SEKIYA

c/o Tsukuba Centre, National Institute of Advanced
Industrial Production and Technology, 1-1 Higashi-1-chome,
30 Tsukuba-shi, Ibaraki-ken, Japan

(74) Agent: 100074505

Patent Attorney T. Ikeura

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(54) Title of the Invention: Azeotropic or azeotrope-like composition
5 comprising fluorine-containing ether and butanols

(57) Abstract

Problem:

To provide novel azeotropic compositions and azeotrope-like
compositions with which there is no loss of the excellent properties such as
10 the cleaning properties and the low toxicity, for example, of the fluorinated
hydrocarbons which contain chlorine and the chlorinated hydrocarbons,
with which there is no concern with respect to the destruction of the ozone
layer and which have little global warming effect.

Means of Resolution:

15 Azeotropic compositions or azeotrope-like compositions which
contain 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane which can
be represented by formula (1) below and at least one type of alcohol
selected from among 2-butanol, isobutanol and t-butanol.

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$$\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3 \quad (1)$$

Scope of the Patent Claims

[Claim 1]

An azeotropic composition or azeotrope-like composition which contains 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and at least one type of alcohol selected from among 2-butanol, isobutanol and t-butanol.

Detailed Description of the Invention

[0001]

Technical Field of the Invention

The invention concerns azeotropic compositions or azeotrope-like compositions, and more precisely the invention concerns azeotropic compositions or azeotrope-like compositions which can be used for flux cleaning, degreasing cleaning, water-cutting drying and as solvents.

[0002]

15

Prior Art

Halogenated hydrocarbons have long been very well known as cleaning solvents for electronic parts, precision machine parts and resin processing parts for example, and they are characterized as a group of hydrocarbons which have been substituted with chlorine atoms or with chlorine atoms and fluorine atoms. These halogenated hydrocarbons have low toxicity and become non-flammable as the number of substituted halogen atoms is increased and they are also both chemically and thermally stable and, moreover, they do not penetrate into the surfaces of plastics and rubbers and provide a level of solubility with is ideal for dissolving waxes and oils and fats and so they are widely used in a variety of industrial fields. For example, the known halogenated hydrocarbons include chlorinated hydrocarbons such as trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane, and freons such as 1,1,2-trichloro-1,2,2-trifluoroethane (freon 113), and the latter freon hydrocarbons in particular have low toxicity and are non-flammable, and both chemically and thermally stable and so they are used in a wide range of fields. However, it has been pointed out that since these fluorinated hydrocarbons which contain chlorine atoms and 1,1,1-trichloroethane do

contain chlorine atoms they have a serious disadvantage in that they destroy the ozone layer in the stratosphere and it has been decided internationally to stop the production and of these materials. Furthermore, trichloroethylene and tetrachloroethylene have resulted in problems with
5 ground water contamination and as a result of subsequent investigation of the state of environmental pollution and as a result of an investigation into their toxicity such as their chronic toxicity it has been ordered that these be designated as class 2 specified chemicals from 1989. In view of these circumstances the development of materials to replace these fluorinated
10 hydrocarbons which contain chlorine and chlorinated hydrocarbons has been carried out actively. At the present time fluorinated compounds which do not contain chlorine atoms are well known as substitute materials. However, compounds of this type lack dissolving power for waxes and oils and fats since they do not contain chlorine atoms. In order to resolve this
15 problem general purpose solvents such as alcohols have been mixed with the substitute compounds with a view to improving the dissolving power, but when mixtures of this type are used as cleaning agent it is known that the liquid composition and the vapour composition are different so that concentration control is required. The azeotropic composition in a mixed
20 composition is such that the vapour composition and the liquid composition are the same, and an azeotrope-like composition is such that they are almost the same, and these are known as useful compositions where concentration control is not required (Japanese Unexamined Patent Application Laid Open H8-268944). However, a mixture does not always
25 have an azeotropic composition, and whether it will or will not have such a composition cannot be predicted.

[0003]

Problems to be Resolved by the Invention

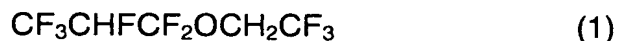
The problem for the present invention is to provide novel
30 azeotropic compositions and azeotrope-like compositions with which there is no loss of the excellent properties such as the cleaning properties and the low toxicity, for example, of the fluorinated hydrocarbons which contain chlorine and the chlorinated hydrocarbons, with which there is no concern

with respect to the destruction of the ozone layer and which have little global warming effect.

[0004]

Means of Resolving These Problems

5 The inventors have realized the present invention as a result of thorough research carried out with a view to resolving the aforementioned problem. That is to say, by means of the present invention there is provided an azeotropic composition or an azeotrope-like composition which contains 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane which can
10 be represented by formula (1) below and at least one type of alcohol selected from among 2-butanol, isobutanol and t-butanol.



[0005]

15 Embodiment of the Invention

 Compositions such as those indicated below are included in practice among the compositions of this invention. Moreover, an azeotropic composition signifies a composition of which the vapour composition and the liquid composition are the same, and with which there is no change in
20 the composition of the composition after repeated vaporization and condensation. Furthermore, an azeotrope-like composition signifies a composition of which the vapour composition and the liquid composition are almost the same, and with which there is only a change of an order which can be neglected in the composition of the composition after
25 repeated vaporization and condensation.

(1) The azeotrope-like compositions comprise from 85.0 to 99.9 wt% of 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and from 0.1 to 15.0 wt% of 2-butanol, and the preferred azeotropic composition comprises 96.98 wt% of 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and
30 3.02 wt% of 2-butanol. The boiling point of this azeotropic composition is 72.13°C at atmospheric pressure (760 mmHg).

(2) The azeotrope-like compositions comprise from 85.0 to 99.9 wt% of 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and from 0.1 to

15.0 wt% of isobutanol, and the preferred azeotropic composition comprises 98.50 wt% of 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and 1.50 wt% of isobutanol. The boiling point of this azeotropic composition is 72.25°C at atmospheric pressure (760 mmHg).

(3) The azeotrope-like compositions comprise from 80.0 to 99.9 wt% of 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and from 0.1 to 20.0 wt% of t-butanol, and the preferred azeotropic composition comprising 88.87 wt% of 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and 11.13 wt% of t-butanol. The boiling point of this azeotropic composition is 70.06°C at atmospheric pressure (760 mmHg).

[0006]

The 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane which is used in this invention is a known substance and it can be synthesized easily by reacting 2,2,2-trifluoroethanol and hexafluoropropene in the presence of a base for example.

[0007]

Various stabilizers may be added to the compositions of this invention when they are to be used under harsh conditions. Stabilizers which are distilled on distillation or which form an azeotrope-like mixture are preferred. Actual examples of such stabilizers include aliphatic nitro compounds such as nitromethane and nitroethane, aromatic nitro compounds such as nitrobenzene and nitrostyrene, ethers such as dimethoxymethane, 1,2-dimethoxyethane, 1,4-dioxane, and 1,3,5-trioxane, epoxides such as glycidol, methyl glycidyl ether, allyl glycidyl ether, phenyl glycidyl ether, 1,2-butylene oxide, cyclohexene oxide and epichlorohydrin, unsaturated hydrocarbons such as hexene, heptene, pentadiene, cyclopentene and cyclohexene, olefinic alcohols such as allyl alcohol and 1-butene-3-ol, acetylene-based alcohols such as 3-methyl-1-butyne-3-ol and 3-methyl-1-pentyne-3-ol, and acrylic acid esters such as methyl acrylate, ethyl acrylate, butyl acrylate and vinyl methacrylate. Moreover, phenols, amines and benzotriazoles can be used conjointly in order to obtain a synergistic stabilizing effect. These stabilizers may be used individually, or

a combination of two or more types may be used. The amount of stabilizer used differs according to the type of stabilizer, but it is of an extent such that the azeotrope-like properties are not affected adversely. The amount used is generally of the order of from 0.01 to 10 wt%, and preferably of the order of from 0.1 to 5 wt%, of the composition of this invention.

[0008]

Furthermore, various surfactants can be added to a composition of this invention, as required, in order to further improve the cleaning power and surface action etc. Examples of such surfactants include non-ionic surfactants such as sorbitan fatty acid esters, for example sorbitan mono-oleate and sorbitan trioleate, polyoxyethylene-sorbitan fatty acid esters, for example polyoxyethylene sorbitan tetra-oleate, polyethylene glycol fatty acid esters, for example polyoxyethylene monolaurate, polyoxyethylene alkyl ethers, for example polyoxyethylene lauryl ether, polyoxyethylene alkylphenyl ethers, for example polyoxyethylene nonylphenyl ether, and polyoxyethylene alkylamine fatty acid amides, for example polyoxyethylene oleic acid amide, and these may be used individually or a combination of two or more types can be used. Cationic surfactants or anionic surfactants can be used conjointly with these non-ionic surfactants with a view to improving the cleaning power and surface action synergistically. The amount of surfactant used differs according to the type, but it is of an order which does not interfere with the azeotrope-like properties, and it is generally of the order of from 0.1 to 20 wt%, and preferably of the order of from 0.3 to 5 wt%, of the composition of this invention.

[0009]

The compositions of this invention can be used in a wide range of known cleaning and drying applications, and in particular they can be used as flux cleaning agents, cleaning solvents, degreasing cleaning agents and water-cutting drying agents and they are very useful as substitutes for the conventional freon 113 and 1,1,1-trichloroethane. Actual examples of such applications include agents for the removal of flux, grease, oil, wax or ink for example, and cleaning agents and water-cutting agents for use with electronic parts (printed circuit boards, liquid crystal displays, magnetic

recording parts, semiconductor materials and the like), electrical machine parts, precision machine parts, resin processing parts, optical lenses and clothing. Methods of cleaning which can be adopted include immersion, spraying, boiling, ultrasonic cleaning and vapour cleaning or a combination of such methods of cleaning. Furthermore, the compositions of this invention can be used in the same ways as in the past in various applications such as solvents for paints, extracting agents, heating media and foaming agents for example.

[0010]

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Illustrative Examples

The characteristic features of the invention are clarified further below by means of illustrative examples. Of course the invention is not limited by these illustrative examples.

[0011]

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Example 1

The vapour/liquid equilibrium and azeotrope point of 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and 2-butanol were measured using vapour/liquid equilibrium measuring apparatus. A mixed sample of a given composition of 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and 2-butanol was introduced into the sample container and heated. The heating was adjusted in such a way as to provide an appropriate dripping rate for the vapour phase condensate and stable boiling was maintained for at least 40 minutes. After confirming that they were stable, the pressure and the boiling point were measured. The liquid phase and the vapour phase were sampled and composition analysis of the liquid samples was carried out using gas chromatography. The results of these measurements are shown in Table 1 and Figures 1 and 2. According to the results the compositions of this invention which contain 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane in an amount ranging from 85.0 to 99.9 wt% and 2-butanol in an amount ranging from 0.1 to 15.0 wt% are azeotrope-like compositions. The composition comprising 96.98 wt% 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and 3.02 wt% 2-butanol is the azeotropic

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composition, and the boiling point at atmospheric pressure (760 mmHg) is 72.13°C.

[0012]

Table 1

CF₃CHFCF₂OCH₂CF₃ + 2-Butanol System

Vapour/liquid equilibrium measurement results at 760 mmHg

	t (°C)	x1 (wt.%)	y1 (wt.%)
1	99.45	0.00	0.00
2	88.79	16.68	66.27
3	79.25	43.63	84.40
4	76.63	64.90	89.43
5	74.70	71.38	90.92
6	73.78	79.19	91.96
7	73.16	88.18	93.30
8	72.86	94.84	93.89
9	72.50	98.28	94.39
10	72.14	99.94	96.28
11	72.14	97.89	97.49
12	72.26	98.81	98.65
13	72.47	100.00	100.00

x1: Concentration of CF₃CHFCF₂OCH₂CF₃ in the liquid phase

y1: Concentration of CF₃CHFCF₂OCH₂CF₃ in the vapour phase

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[0013]

Example 2

The same procedure as in Example 1 was followed except that isobutanol was used instead of 2-butanol. The results obtained are shown in Table 2 and Figures 3 and 4. According to the results the compositions of this invention which contain 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane in an amount ranging from 85.0 to 99.9 wt% and isobutanol in an amount ranging from 0.1 to 15.0 wt% are azeotrope-like compositions. Here the composition comprising 98.50 wt% 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and 1.50 wt% isobutanol is the azeotropic composition, and the boiling point at atmospheric pressure (760 mmHg) is 72.25°C.

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[0014]

Table 2
 $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ + Isobutanol System
 Vapour/liquid equilibrium measurement results at 760 mmHg

	t (°C)	x1 (wt.%)	y1 (wt.%)
1	107.79	0.00	0.00
2	88.07	28.82	81.97
3	78.77	45.91	90.74
4	76.08	58.88	92.86
5	75.07	66.93	93.54
6	74.45	74.19	94.08
7	74.03	78.52	94.43
8	73.92	81.86	94.58
9	73.66	85.29	94.88
10	73.25	88.83	95.25
11	72.96	90.70	95.61
12	72.64	94.82	96.12
13	72.32	96.87	97.19
14	72.25	98.01	98.11
15	72.33	99.21	99.15
16	72.47	100.00	100.00

5

x1: Concentration of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ in the liquid phase

y1: Concentration of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ in the vapour phase

[0015]

10 Example 3

The same procedure as in Example 1 was followed except that t-butanol was used instead of 2-butanol. The results obtained are shown in Table 3 and Figures 5 and 6. According to the results the compositions of this invention which contain 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane in an amount ranging from 80.0 to 99.9 wt% and t-butanol in an amount ranging from 0.1 to 20.0 wt% are azeotrope-like compositions. Here the composition comprising 88.87 wt% 1,1,1,2,3,3-hexafluoro-3-(2,2,2-trifluoroethoxy)propane and 11.13 wt% t-butanol is the azeotropic composition, and the boiling point at atmospheric pressure (760 mmHg) is 70.06°C.

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[0016]

Table 3
 $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ + t-Butanol System
 Vapour/liquid equilibrium measurement results at 760 mmHg

	t (°C)	x1 (wt. %)	y1 (wt. %)
1	82.97	0.00	0.00
2	78.57	19.00	44.97
3	77.60	23.39	61.86
4	76.88	27.26	66.89
5	76.12	31.71	69.57
6	75.52	35.83	62.75
7	74.27	44.15	68.14
8	73.08	51.89	72.43
9	72.09	59.46	76.92
10	71.72	62.32	78.38
11	71.17	68.32	80.67
12	70.63	73.47	82.80
13	70.23	82.63	85.44
14	70.12	86.24	87.31
15	70.06	88.87	88.87
16	70.20	91.01	90.17
17	70.28	91.87	90.74
18	70.44	93.00	92.03
19	70.50	94.31	92.78
20	70.70	95.95	93.70
21	71.65	98.90	97.35
22	72.47	100.00	100.00

5

x1: Concentration of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ in the liquid phase
 y1: Concentration of $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ in the vapour phase

[0017]

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Effect of the Invention

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The compositions of this invention have excellent properties such as cleaning properties similar to those of freon and the chlorinated hydrocarbons and low toxicity and, moreover, by using these compositions it is possible to greatly reduce the environmental burden in terms of the destruction of the ozone layer and global warming when compared with that imposed by the freons and the chlorinated hydrocarbons which have been used in the past.

Brief Explanation of the Drawings

Figure 1 shows the $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ concentration in the liquid phase (x_1)/ the concentration of the said substance in the vapour phase (y_1) curve for the vapour/liquid equilibrium state of the said substance + 2-butanol system.

Figure 2 shows the $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ concentration in the liquid phase (x_1)/temperature (t) curve for the vapour/liquid equilibrium state of the said substance + 2-butanol system.

Figure 3 shows the $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ concentration in the liquid phase (x_1)/ the concentration of the said substance in the vapour phase (y_1) curve for the vapour/liquid equilibrium state of the said substance + isobutanol system.

Figure 4 shows the $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ concentration in the liquid phase (x_1)/temperature (t) curve for the vapour/liquid equilibrium state of the said substance + isobutanol system.

Figure 5 shows the $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ concentration in the liquid phase (x_1)/ the concentration of the said substance in the vapour phase (y_1) curve for the vapour/liquid equilibrium state of the said substance + t-butanol system.

Figure 6 shows the $\text{CF}_3\text{CHFCF}_2\text{OCH}_2\text{CF}_3$ concentration in the liquid phase (x_1)/temperature (t) curve for the vapour/liquid equilibrium state of the said substance + t-butanol system.

Figure 1

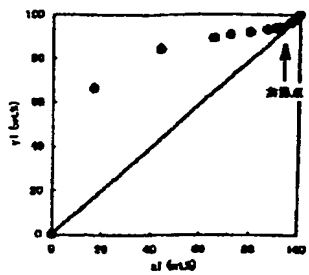


Figure 2

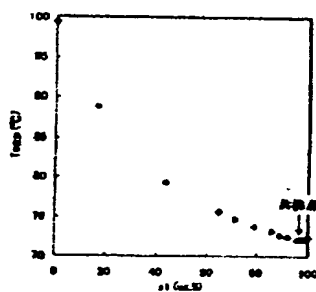


Figure 3

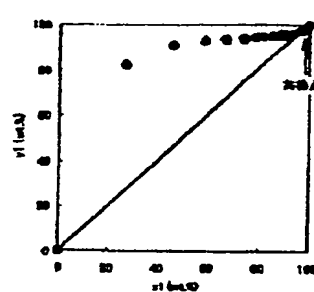


Figure 4

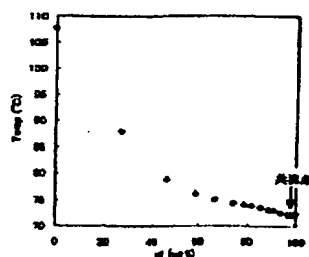


Figure 5

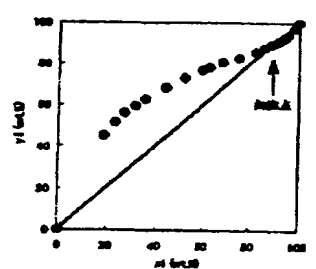


Figure 6

